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Sorption-enhanced Steam Methane Reforming for Combined CO_2 Capture and Hydrogen Production: A *State-of-the-Art* Review

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ABSTRACT

The European Commission have just stated that hydrogen would play a major role in the economic recovery of post-COVID-19 EU countries. Hydrogen is recognised as one of the key players in a fossil fuel-free world in decades to come. However, commercially practiced pathways to hydrogen production todays, are associated with a considerable amount of carbon emissions. The Paris Climate Change Agreement has set out plans for an international commitment to reduce carbon emissions within the forthcoming decades. A sustainable hydrogen future would only be achievable if hydrogen production is "designed" to capture such emissions. Today, nearly 98% of global hydrogen production relies on the utilisation of fossil fuels. Among these, steam methane reforming (SMR) boasts the biggest share of nearly 50% of the global generation. SMR processes correspond to a significant amount of carbon emissions at various points throughout the process. Despite the dark side of the SMR processes, they are projected to play a major role in hydrogen production by the first half of this century. This that a sustainable, yet clean short/medium-term hydrogen production is only possible by devising a plan to efficiently capture this co-produced carbon as stated in the latest International Energy Agency (IEA) reports. Here, we have carried out an in-depth technical review of the processes employed in sorption-enhanced steam methane reforming (SE-SMR), an emerging technology in *low-carbon* SMR, for combined carbon capture and hydrogen production. This paper aims to provide an in-depth review on two key challenging elements of SE-SMR i.e. the advancements in catalysts/adsorbents preparation, and current approaches in process synthesis and optimisation including the employment of artificial intelligence in SE-SMR processes. To the best of the authors' knowledge, there is a clear gap in the literature where the above areas have been scrutinised in a systematic and coherent fashion. The gap is even more pronounced in the application of AI in SE-SMR technologies. As a result, this work aims to fill this gap within the scientific literature.

Introduction

Today, climate change is known to be the biggest, yet immediate threat to our world's ecosystem. On December 12, 2015, at the COP21, the world saw the commitment of 197 countries to navigating the impacts of climate change (as of today, 189 countries have joined the Agreement). The Agreement now requires the countries to limit their greenhouse gas (GHG) emissions so the global temperature rise is limited to 2°C by the end of this century (with an aspiration of 1.5°C). The COP21 has been the first tangible international move towards a *low-carbon future* which sets out a practical pathway to meet the United Nation's Sustainable Development Goals (The Paris Agreement 2021). In the UK, and as a result of sustained public pressure in the country in the early summer of 2019, the UK government's response was to declare a climate emergency in June, thereby, announcing a target of net zero greenhouse gas emissions compared to the 1990 levels by the year 2050 (Petrovic et al., 2021, Stark and Thompson, 2019). More recently, in November 2020, the UK government announced its *10-point plan* which aims to "mobilise £12b of government investment, and potentially 3 times as much from the private sector, to create and support up to 250,000 green jobs" (UK Government 2021).

Anthropogenic carbon (CO_2) emissions (over 40 billion tonnes per year - mostly arising from the combustion of fossil fuels) play a key role in the global temperature rise as seen today. In 2018, electricity and

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heat production (~13.9b tons), transport (~8.2b tons), and manufacturing industries and constructions (~6.2b tons) and building (2.9b tons), contributed to the biggest of such shares globally (International Energy Agency (IEA) 2018). With fossil fuels currently responsible for 80% of the global primary, meeting the COP21 climate change target would require a 60% reduction in carbon emission from both energy and industrial sectors (Safari and Dincer, 2020). Consequently, it is now becoming urgent for an accelerated global shift towards low-carbon technologies in order to meet the Climate Change targets. Although renewable energies, such as solar and wind and clean fuels (e.g. hydrogen), together with advanced energy storage devices (e.g. batteries and hydrogen (as the energy storage medium (a synthetic energy carrier) for renewables (Yan et al., 2020))) are promising "longer-term" solutions to a *low-carbon* world, it has been projected that a rapid reduction in consumption of fossil fuels in the developing worlds is a much bigger challenge compared to their developed counterparts. As a result, preventing the carbon emission at the emission source (e.g. flue gases associated with power/industry sectors) is an anticipated short- to mid-term solution to atmospheric carbon reduction. The European Commission has referred to carbon capture and storage (CCS) as "priority breakthrough technology" in their Green Deal, encouraging new funding within the post COVID-19 recovery package (van Renssen, 2020). In the UK, the 8th point of the recently announced *10-point plan*, is specifically dedicated to CCS. Taking steps into the future, we are now at the crossroads of renewables, clean fuels and carbon capture, utilisation and storage (CCUS) technologies. These technologies are required to move hand in hand for us to be able to meet the soaring global energy demands and also, to paint a more realistic picture of a *low-carbon* future in decades to come. Among the most feasible roadmaps, hydrogen (H_2) appears to show off excellent potentials in taking the lead in serving as a commercially viable clean fuel of the future.

The Role of Hydrogen in Low-carbon *Economy*

Hydrogen was considered an alternative fuel under the Energy Policy Act of 1992 in the United States. The energy in one kilogram of hydrogen gas is approximately equal to the energy in 2.8 kilograms of petrol (van Renssen, 2020). Nevertheless, despite the lower *volumetric* energy density and unlike conventional fossil fuels, the combustion of hydrogen does not lead to the production of any carbon dioxide (or GHG for that matter), making its utilisation, one of the most practical pathways in carbon emission reduction within the energy and power sectors' contexts. In addition, hydrogen is a key building block in the manufacture of many chemicals e.g. ammonia and methanol (Ohs et al., 2019). Hydrogen is an integral part of all the eight European Commission's net zero emission scenarios for 2050 (van Renssen, 2020, European Commission 2018); in principle, hydrogen not only can be used as a means to energy storage (i.e. the surplus of renewable energies), but it can also be used in replacement of fossil fuels in chemicals and fuels production, yet boasting its carbon neutrality (van Renssen, 2020). More recently, the European Commission have just stated that hydrogen would play a major role in the economic recovery of post-COVID-19 EU countries (European Commission 2020). Despite hydrogen being classed as a *low-carbon* fuel, its main production routes are associated with a high amount of carbon emissions.

Currently, hydrogen *production* is responsible for putting about 830m tonnes of CO_2 into the atmosphere (Rozyyev et al., 2019). Although the main commercial route to hydrogen production in the steam-methane reforming process, hydrogen can be also produced *via* electrolysis, thermolysis, biomass gasification, bio-catalysis or fermentative routes (Shamsudin et al., 2019). Depending on the adopted process, three main classes of hydrogen can be identified: grey hydrogen (i.e. *via* reforming fossil fuels (Challiwala et al., 2017)), blue hydrogen (i.e. with carbon captured, utilised or stored - CCUS) and green hydrogen (i.e. *via* the utilisation of a renewable feedstock as well as renewable energy source such as wind and solar, nuclear, geothermal, biomass and hydropower (Atilhan et al., 2021)). Depending on the production route, the total carbon emissions could be considerably reduced (Figure 1).

Hydrogen: Current Global Production Status via *Various Routes*

The global hydrogen market is forecast to increase from 70m tonnes in 2019 to 120m tonnes in 2024 (Safari and Dincer, 2020, Atilhan et al., 2021). Green hydrogen is currently mostly produced *via* water splitting (e.g. water electrolysis, water thermolysis, photocatalytic water splitting, and thermochemical water splitting) or *via* dehydrogenation of hydrogen carrier molecules (Atilhan et al., 2021, Wang et al., 2019). The production of green hydrogen, however, is yet to overcome a number of technological and economical barriers and therefore, is not currently widely considered to be a viable option for large-scale deployment. Nevertheless, it is expected that the total cost of green hydrogen would drop by 70% by the end of the next decade (Atilhan et al., 2021). Global green hydrogen production capacity by region is illustrated in Figure 2.

The latest IEA report indicates that more than 95% of the world's hydrogen demand is met *via* the reforming of fossil fuels (at ~76.5m tonnes in 2019) out of which more than half is generated *via* steam-methane reforming (The Future of Hydrogen 2019). Grey hydrogen processes inherently correspond to significant carbon emissions around the world. However, when retrofitted/coupled with carbon capture, they can contribute to a significant reduction in carbon emissions. The downside, however, is the fact that blue hydrogen production is closely linked to the viability of locational carbon storage upon capture and therefore, depends on regional regulations. Nevertheless, within the EU, a growing number of countries are aiming to set a minimum carbon price (penalty or tax) that will continue to increase to about €30 to €40 per ton of CO_2 over the next 10 years. This means that the cost of CO_2 could eventually add almost €0.50 to the price of a kilo of grey hydrogen in Europe, bringing the total price to around €2 (van Hulst, 2019). This is seen as a great incentive to accelerate towards blue/green hydrogen in the short/long-terms. On the other hand, the cost of blue hydrogen is a function of the cost of natural gas as well as the cost of carbon capture (currently set at about €50-€70/t_{CO2} in the EU). This means that the cost of blue hydrogen is higher than the cost of its grey counterpart. However, this gap is forecast to shrink with time IF the price of CO_2 emission (i.e. carbon tax) rises accordingly (van Hulst, 2019). The implementation of effective policies such as European Renewable Energy Directive (REDII) would also help to facilitate the deployment of such technologies throughout the EU.

Motivation and Paper's Roadmap

There have been only a few review articles on *hydrogen production with carbon capture* published within the past decade. The most recent of these is the work of Voldsund. et al. (Voldsund et al., 2016) who discussed the various routes to hydrogen production with CO_2 capture with a very brief section on sorption-enhanced steam-methane reforming (SE-SMR). A more recent, yet highly focused review paper was published in 2018 by Giuliano and Gallucci (di Giuliano and Gallucci, 2018) who presented an extensive discussion on the SE-SMR based on nickel and calcium looping. To the best knowledge of the authors, there has been no technical review paper which revolves around SE-SMR which discusses the application of various catalysts employed in SE-SMR and their efficiencies, nor any review article that comprehensively probes into the impact of various SE-SMR process designs on the overall feasibility/viability of the process. More importantly, despite the growing interest and published works on the employment of artificial intelligence (AI) in process optimisation, there exists no review paper that has comprehensively discussed such an important aspect in SE-SMR processes – a key missing elements in this research area. As a result, this review aims to scrutinise the most recent developments in the realms above, and address the existing research gaps in the scientific literature. In this work, we have painstakingly reviewed 137 indexed research papers and

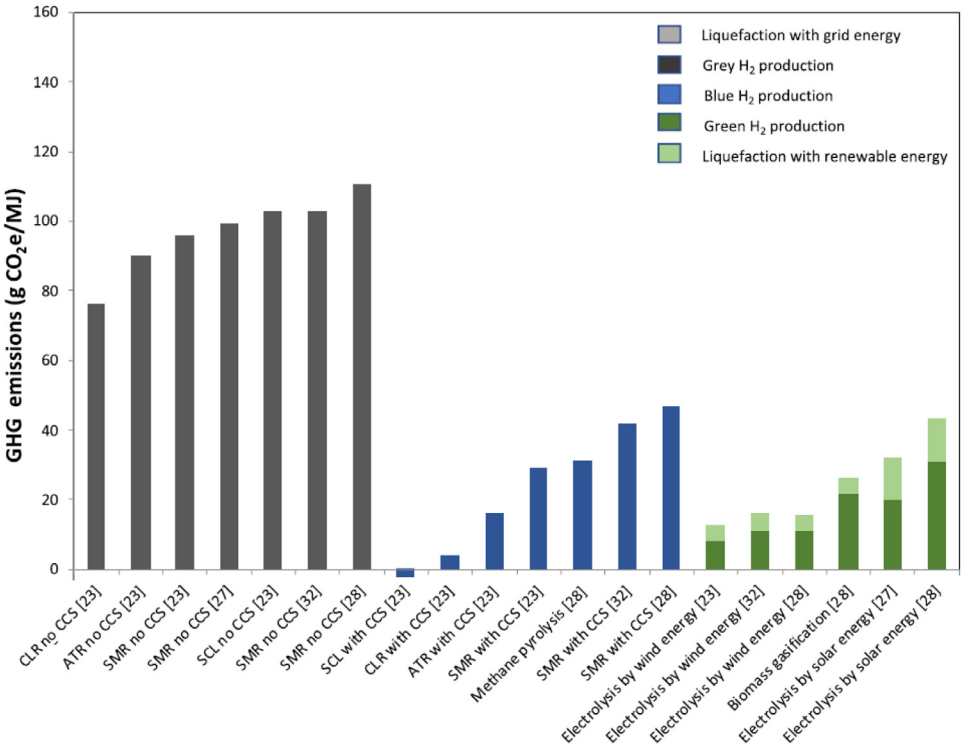

Figure 1. GHG emission data corresponding to various routes in hydrogen production – figure retrieved from: (Atilhan et al., 2021).

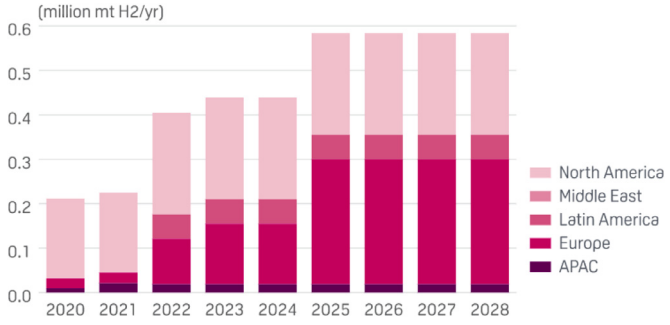

Figure 2. Regional global green hydrogen production – figure retrieved from: (Robinson, 2020).

conference proceedings on and around the topic published in the recent years.

SE-SMR: *Process Overview and Current Status*

The need for hydrogen in the United States alone was projected to exceed 5,300 billion standard cubic feet (scf) by 2021 (Mays, 2017). As a result, there is an imminent need to not only increase the number of *low-carbon* production sites (e.g. SMR emits 8 –12 tonnes of CO_2 per tonne of H_2 produced (The Future of Hydrogen 2019)), but also to intensify the current SMR plants. Figure 3 illustrates a simplified schematic of a conventional SMR process with carbon capture.

In a typical conventional SMR process (Figure 3), the feedstock is introduced into the reformer (having initially undergone compression and heating), where the reforming of methane occurs as shown in Eq. 1. Since this reaction is endothermic, heat has to be supplied to surpass the thermodynamic energy barrier. The produced syngas is then carried to the shift converter, where the water-gas shift (WGS) reaction takes place (Eq. 2). Both of the reactions benefit greatly from presence of specific catalysts (classically Ni-based), which are discussed at length in Section 3 of this paper.

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \Delta H_{298} = \ 206.4\ kJ.mol^{-1} \quad (1)$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \Delta H_{298} = \ -41.1\ kJ.mol^{-1} \quad (2)$$

Following complete (or rather nearly complete) conversion of the fuel into H_2 and CO_2, the purification processes proceeds. The conventional SMR process normally utilises amine scrubbing as means to turn the hydrogen from “brown/grey” to “blue”. Further downstream pressure swing adsorption (PSA) is applied to purify the H_2 to the commercial standards. This established technology has proven its worth and has been employed for decades, though, there are limitations such as the high pressure and temperature requirements, and low yield of the desired product (usually below 80%) which could be improved, hence, paving the way for a rapid increase in wide-spread utilisation and implementation of hydrogen as an energy carrier.

One possible route to increasing the yield of the conventional SMR process, is a shift in the equilibrium of the reactions (i.e. the Le-Chatelier’s principle) by extracting CO_2 out of the “equation”. Therefore, integrating carbon capture unit with the reforming reactor would not only lead to a reduction of capital cost (CAPEX) of the operation (a more compact (2-in-1) process unit), but also increase the productivity and output of the reformer itself. Additionally, this would allow for more moderate operating conditions (from a temperature of 800 – 1000°C and a pressure of 1.53 MPa for traditional SMR (di Giuliano and Gallucci, 2018) leading to approximately 70% of H_2 in the product (Wang et al., 2021), to 450 – 490°C and 180 – 890 kPa, resulting in the production of a gas stream with 90 – 98% hydrogen for SE-SMR (Cherbanski and Molga, 2018)), thereby, potentially lowering the operational expenses (OPEX) overall. A schematic for a generic SE-SMR process can be seen in Figure 4.

SE-SMR is currently at the technology readiness level (TRL) 4. This is evidenced by the available publications in the literature on experimental studies (Cherbański and Molga, 2018, Johnsen et al., 2006, Arstad et al., 2012, Ding and Alpay, 2000, Zhang et al., 2016) and process simulations (Yan et al., 2020, Ochoa-Fernández et al., 2007, Nkulikiyinka et al., 2020, Cobden et al., 2007, Yan et al., 2020) alike. Pilot-plant studies would be the next step in taking the TRL to the next level. In a recent move in this direction, Cranfield University together with Gas Technol-

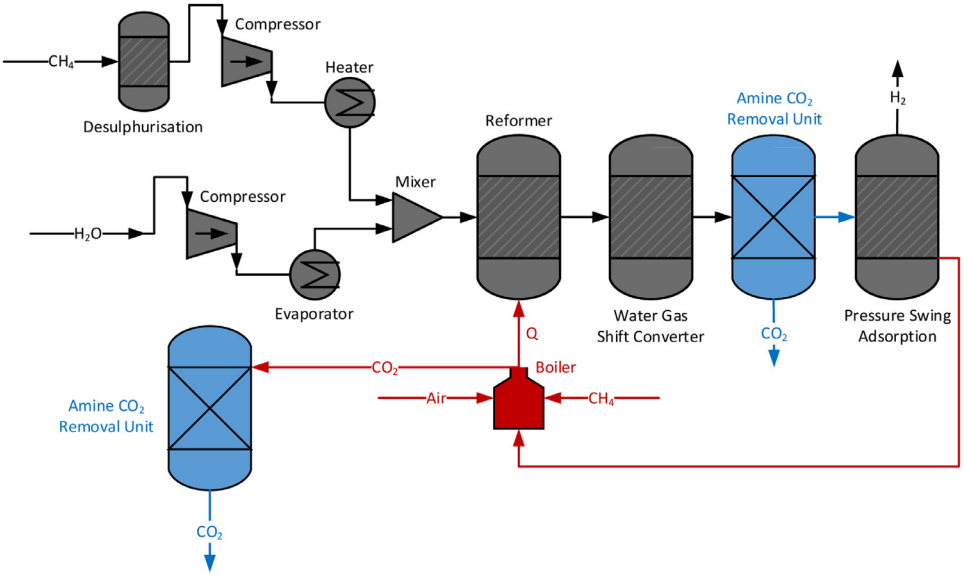

Figure 3. Process flow diagram for a conventional SMR process with CO_2 capture. The grey coloured sections correspond to the grey (and brown) hydrogen production process, whereas the blue represents the additional carbon capturing units required to achieve the net-zero emissions targets, and the red colour denotes the boiler, supplying heat to the reformer whilst simultaneously emitting additional carbon dioxide.

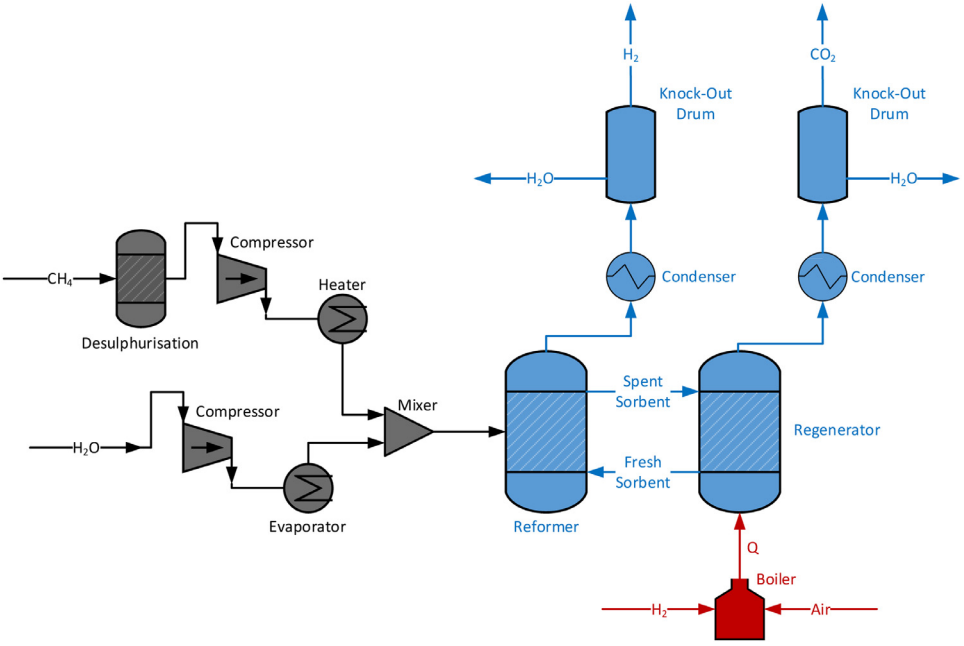

Figure 4. Process flow diagram for a typical SE-SMR. The grey coloured sections correspond to same units as in the convention SMR process (that produces grey (and brown) hydrogen), whereas the blue represents the innovative solutions of SE-SMR, turning the grey (or brown) hydrogen into blue, and the red colour denotes the boiler that is fired by H_2 (and may also use oxy-fuel combustion), thus not emitting additional carbon dioxide.

ogy Institute (GTI), Doosan Babcock and the UK Department for Business, Energy and Industrial Strategy's Energy Innovation programme are currently constructing a 1.5 MW_{th} pilot plant to further develop the process (scheduled to be completed in Autumn 2021), aiming to lift the TRL up, to 6 (The Future of Hydrogen 2019). This system will utilise a bubbling fluidised bed reactor for the reformer (that would simultaneously act as a carbonator), and an entrained flow reactor for the calciner (Figure 5). In comparison with the commercialised processes with a CCS unit at "tail end", operating at 24 bar absolute (bara), the constructed system could achieve a ~20% reduction in the levelized cost of hydrogen (LCOH) combined with an over 50% reduction in CAPEX and OPEX, whilst maintaining a CO_2 capture rate of approximately 96%, producing the same H_2 purity (HyPER 2021).

A similar plant has been constructed by GTI in California, USA (Mays, 2017), achieving 20,000 scf/day (approximately 71 kW_{th}, i.e. 20 times less than the currently under construction pilot plant in the UK) of product with an H_2 purity of >80%. In this process, an 18% reduction in CO_2 emissions, 12 – 40% in CAPEX and 20% OPEX savings in comparison to the conventional SMR process have been reported. Furthermore, the cost per tonne of CO_2 captured was reduced from 83.02 \$/tCO_2 (95.61 \$/tCO_2 if accounting for Transmission Storage and Monitoring (TS&M)) for a traditional SMR with an amine-scrubbing unit, to a mere 16.82 \$/tCO_2 captured (or 28.68 \$/tCO_2 with TS&M).

The argument for SE-SMR over conventional SMR is growing ever-stronger with more projects coming to fruition and depicting the vast environmental benefits of adding a sorbent into either the water-gas shift reactor (SE-WGS) or the reformer (SE-SMR). However, the main goal of such system is to produce hydrogen and this process requires the presence of catalyst to be commercially viable. In order to maximise the benefits of "both worlds", a combined sorbent-catalyst material is preferred. This approach allows for myriad favourable synergies and improvements as outlined in the literature (di Giuliano and Gallucci, 2018, Wang et al., 2021). In the following section, we discuss the breakthroughs made in the realm of catalyst synthesis for SE-SMR processes within the past few years. As the catalysts used in SE-SMR and

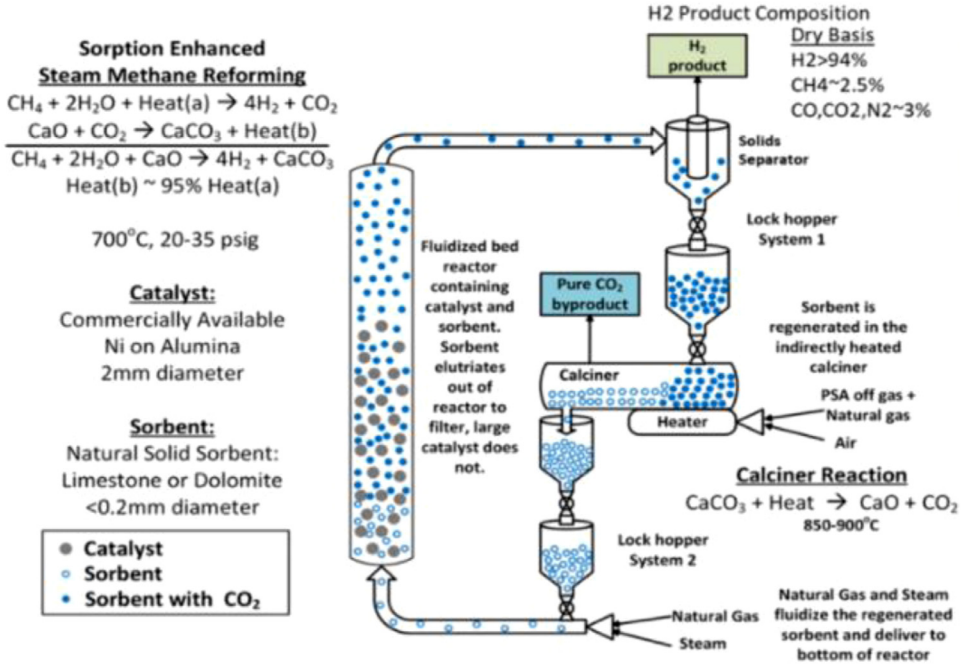

Figure 5. The 1.5 MWth pilot system – figure retrieved from (The Future of Hydrogen 2019).

SMR processes are inherently identical, we have adopted a holistic approach in this section.

Catalysts and Sorbents: State-of-the-Art of Advanced Catalysts and Sorbents Used in (SE)-SMR

Application of Catalysts in (SE)-SMR Processes

Catalysts play a crucial role in both the steam-methane reforming (SMR) and the water-gas shift (WGS) reactors. Although SMR and WGS are established processes, lots of work on catalyst development and modifications is still ongoing to improve the conversion efficiency, reduce operating temperatures, and improve the life-time of catalysts. In SMR, both noble and non-noble metals have shown good catalytic properties. One of the major drawbacks in SMR is catalyst poisoning due to coking during methane conversion to CO. Among noble metals, the catalytic activity for SMR has been proposed in the order Ru > Rh > Ir > Pt (Jones et al., 2008). However, owing to high cost of the noble metals, industrially, nickel-based catalyst is the preferred choice. Ni-based catalysts are comparatively cheaper and have shown a catalytic performance similar to Ir and Pt. In Ni-based catalysts, the major issues are related to (i) catalytic activity, (ii) sulphur poisoning, (iii) carbon formation, and (iv) sintering which reduce the process efficiency with time, and therefore, research in relegating these detrimental effects have been the main focus in the last decade.

In order to reduce the effects of poisoning and improve the conversion efficiency in Ni-based catalysts, the use of catalyst promotors and catalyst supports have been investigated (Sekine et al., 2011, Matsumura and Nakamori, 2004, Nieva et al., 2014). Metal oxides are the preferred choice as catalyst support. Nieva et al (Nieva et al., 2014) studied the influence of support on Ni-based catalysts for SMR reaction at 600°C from which the activity order was found to be: $Ni/MgAl_2O_4$ > $Ni/ZnAl_2O_4$ > Ni/Al_2O_3 > Ni/SiO_2. In the case of Ni/SiO_2, surface oxidation and carbon deposition were observed, which led to deactivation of the catalyst. However, the $Ni/MgAl_2O_4$ did not show any detrimental effect at high temperatures. Oxides such as SiO_2 and Al_2O_3 were found to be very stable at high temperatures and acted as barriers for fast nickel oxidation. Compared to these oxides, rare-earth metal oxides with nickel catalyst not only showed improvement towards inhibiting nickel oxidation, but also promoted higher methane conversion. In particular, CeO_2, ZrO_2 and La_2O_3 showed excellent Ni-support catalyst to promote methane conversion due to their unfilled *d* orbitals, which facilitates the catalytic reactions (Matsumura and Nakamori, 2004, Wang et al., 2014, Xu et al., 2006, Dan et al., 2012).

Besides catalyst support, the crystallography of the Ni catalyst and the catalyst support also plays an important role in reducing the energy barrier for methane conversion. Methane conversion to hydrogen over a catalyst includes various reaction steps with several possible pathways which is still under debate (Nikolla et al., 2009, Meloni et al., 2020, Xu et al., 2013, Rostrup-Nielsen and Nørskov, 2006). However, it has been identified that for nickel catalysts, (211) facet is the most active sites to promote methane conversion. Figure 6a compares the energy diagram of SMR which shows a dramatic decrease in activation barrier in the case of Ni (211) during various conversion steps. Comparing the two nickel facets, it is clear that graphene is formed in one case, lowering the energy barrier compared to the formation of carbon for Ni (111). This graphene formation was confirmed using *in situ* transmission electron microscopy (TEM) (Helveg et al., 2004). However, the presence of other carbon contamination detriments the catalytic performance and therefore, rendering the modification of nickel surface essential. Figure 6b shows the influence of alloying nickel with other metals with respect to methane conversion. The turnover frequency (TOF) of rather inexpensive Ni, Fe and Co alloys, show a higher activity and stability under industrial inlet conditions of 638 K and a pressure of 14.3 bar with an inlet gas composition of 14.5% CH_4, 83.1% H_2O, 0.1% CO, 0.4% N_2 and 1.0% H_2.

Based on the reported calculations, the authors concluded that A_3B type alloys, specifically, Ni_3Fe and Co_3Ni, would be good candidates for steam reforming reactions at high temperatures.

Interestingly, Du et al (Du et al., 2012) showed that besides the crystallography of Ni, the crystallography of the catalyst support also played an important role in the catalytic activity. For the case of Ni-CeO_2 catalyst, high catalytic activity and higher coke resistance was observed when (110) and (100) planes of CeO_2 was exposed to the reaction compared to the more stable (111) plane. The study by Du et al and other researchers opens up a new question regarding the contribution of the metal/metal oxide interface which would inevitably play an important role in the catalytic activity, carbon formation, sulphur poisoning and

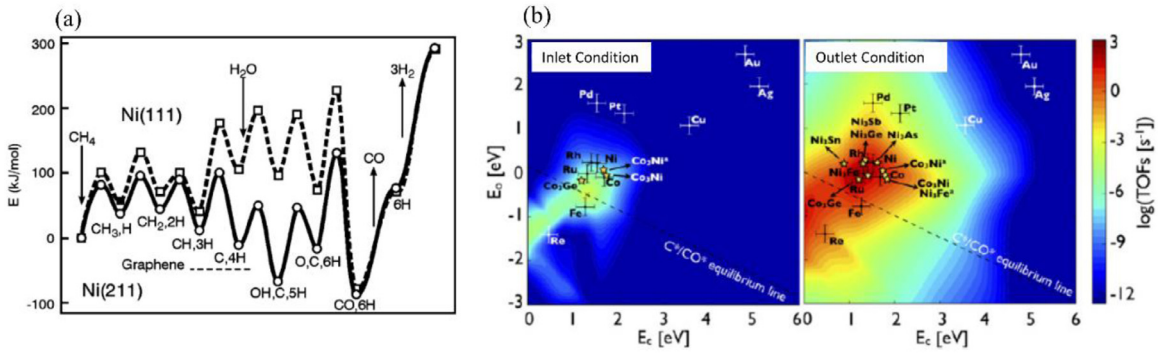

Figure 6. (a): DFT calculation showing the energy diagram for steam reforming of methane adopted from (Rostrup-Nielsen and Nørskov, 2006) (b): Calculated TOF for CO production adopted from (Xu et al., 2013).

sintering and therefore are being intensively studied in the last couple of years both by theory and *in situ* experimental characterisation techniques (Rodriguez et al., 2017).

Reaction Kinetics in (SE)-SMR Processes

In SMR, catalysts describe pathways to bring down the energy consumption to its theoretical values. However, equally important is the kinetics and reaction mechanism of the process which has not been well covered in literature. In 1979, Temkin (Temkin, 1979) was the first to look into the kinetics of SMR process over nickel with varying temperature (450-900 °C) and found that a first order reaction takes place at higher temperature whereas, a delay in rate of hydrogen formation occurred at lower temperatures. The model was further improved by Xu and Froment (Xu and Froment, 1989, Xu and Froment, 1989) and they identified three main reactions and formulated the rate of reaction expression as shown in Eq. 3-5.

$$r_1 = \frac{p_{H_2}^{k_1/2.5}\cdot\left[p_{CH_4}\cdot p_{H_2O} - \frac{p_{H_2}^3\cdot p_{CO}}{K_{eq1}}\right]}{\left(1 + K_{CO}\cdot p_{CO} + K_{H_2}\cdot p_{H_2} + K_{CH_4}\cdot p_{CH_4} + K_{H_2O}\cdot\frac{p_{H_2O}}{p_{H_2}}\right)^2} \quad (3)$$

$$r_2 = \frac{p_{H_2}^{k_2}\cdot\left[p_{CO}\cdot p_{H_2O} - \frac{p_{H_2}\cdot p_{CO_2}}{K_{eq2}}\right]}{\left(1 + K_{CO}\cdot p_{CO} + K_{H_2}\cdot p_{H_2} + K_{CH_4}\cdot p_{CH_4} + K_{H_2O}\cdot\frac{p_{H_2O}}{p_{H_2}}\right)^2} \quad (4)$$

$$r_3 = \frac{p_{H_2}^{k_3/3.5}\cdot\left[p_{CH_4}\cdot p_{H_2O}^2 - \frac{p_{H_2}^4\cdot p_{CO_2}}{K_{eq3}}\right]}{\left(1 + K_{CO}\cdot p_{CO} + K_{H_2}\cdot p_{H_2} + K_{CH_4}\cdot p_{CH_4} + K_{H_2O}\cdot\frac{p_{H_2O}}{p_{H_2}}\right)^2} \quad (5)$$

Where k_i is the rate coefficient of the reactions, K_i is adsorption constant, $K_{eq,i}$ is the equilibrium constant of the reaction, and p is the partial pressure of different gases. Further modification in the rate equation and SMR reaction mechanism were established in later years, mostly focussing the attention on the rate expression due to contradicting results.

Using experimentally parameterized microkinetic model, it was shown for both nickel and Ni/La_2O_3 catalyst that the rate limiting steps of SMR was the adsorption of CH_4, followed by cracking and reactions between carbon and oxycarbonate species (Tsipouriari and Verykios, 2001), (Aparicio, 1997). Later, based on kinetic and isotopic measurements on Ni/MgO catalyst, Wei and Iglesia (Wei and Iglesia, 2004) showed that methane chemisorption is the main rate limiting step in SMR and the rate of reaction is insensitive to hydrogen and water partial pressures at high temperatures. More recently, using a combined modelling and experiment, it was shown that the availability of surface oxygen plays a key role in determining the rate of conversion of methane (Maier et al., 2011). Several studies with different metal/metal oxide catalysts were also investigated for SMR which resulted in different kinetics expressions (Iulianelli et al., 2016, LeValley et al., 2014). The kinetic expression differed as a result of different systems studied including the particle size, support catalyst and the dispersion of metal in the catalyst (Jones et al., 2008, Iulianelli et al., 2016, Ligthart et al., 2011, Wang et al., 2009). However, although the systems considered were different, the rate limiting step were always found to be related to methane activation, or adsorption.

Water-Gas Shift Reactions in (SE)-SMR Processes

WGS reaction is an exothermic reaction and therefore, lower temperatures favour higher conversions. However, the reaction kinetics is slow, and in order to improve reaction kinetics, a high-temperature process is required. Therefore, in a typical industrial scenario to balance the thermodynamics and kinetics, a high temperature WGS process followed by low temperature WGS counterpart, with different catalysts, are typically employed. The different catalysts for WGS can be classified as:

1 High temperature catalysts (metal alloys, metal oxides)
2 Low temperature catalysts (metal alloys, metal hydroxides)
3 Carbon based catalysts
4 Ceria based noble metal catalysts
5 Nanostructured catalysts

High temperature catalysts operate in the range of 300-350 °C, where Fe-Cr oxide-based alloys are typically employed. Typical composition of the catalyst is 74.2% Fe_2O_3 and 10% Cr_2O_3 with rest being volatiles and MgO (Newsome, 1980). The typical life of the catalyst ranges between 3 and 5 years mainly due to sintering effects and poisoning of the catalyst which adversely impact the number of the active sites. Another important factor in the improvement of catalytic performance and catalysts' lifetime, is to maintain CO-to-steam ratio based on Eq. 6.

$$R = \left(\frac{\{[CO] + [H_2]\}}{\{[CO_2] + [H_2O]\}}\right) \quad (6)$$

If the CO-to-steam ratio is high, reduction of Fe_2O_3 to FeO and Fe can take place which diminishes the catalytic effect and therefore, the R factor is approximately maintained at 1 (Yu et al., 2006, Rhodes et al., 1995). Improvements in Fe-based catalysts have been studied by replacing Cr by Al or V and *via* the addition of catalytic promotors such as B, Cu, Ag, Ba, Pb and Ce (de Araújo and do Carmo Rangel, 2000, Ladebeck and Kochloefl, 1995). Some promoters such as B have been found to negatively impact the activity. Among various promoters the catalytic activity is shown to increase in the order of: Hg>Ag>Ba>Cu>Pb (Rhodes et al., 2002). Based on various studies, it can be deduced that the presence of catalyst promoters, and the incorporation of Al and Cu in the Fe-based catalysts promote the magnetite phase formation and stabilisation without undergoing further reduction to FeO and metallic Fe.

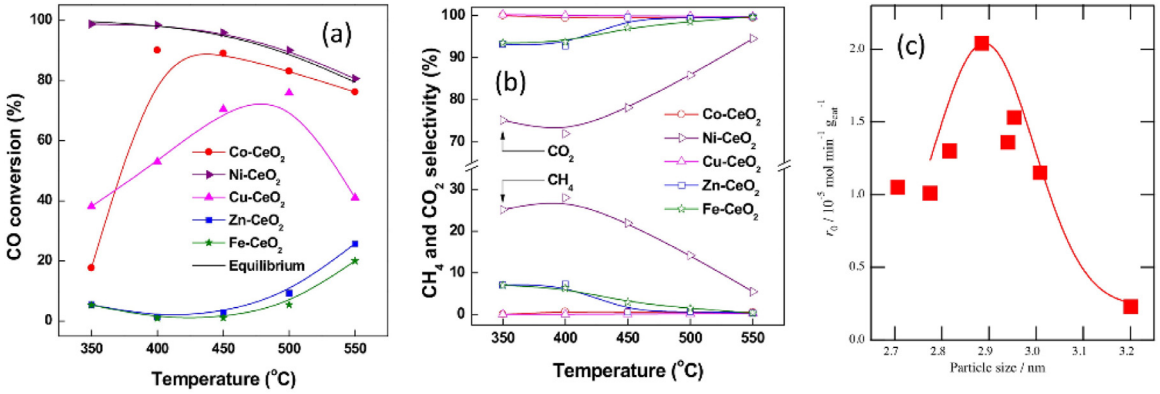

Figure 7. WGS activity of (a) CO conversion with various metal supported on CeO_2 as a function of reaction temperature (b) selectivity to CH4 and CO_2 reproduced with permission from (Jha et al., 2016) (c) effect of nickel nanoparticles size (Kitagawa et al., 2014).

Besides Fe-based catalysts, Ni-based solid solutions are another category of catalyst which have shown great promise (Ashok et al., 2018). However, challenges lie to modify the nickel catalyst to supress the promotion of methanation reactions. Various studies showed that the size of nickel nanoparticles, the presence of catalyst support, and doping and alloying of nickel can help in promoting the catalyst and supress methanation process (Ashok et al., 2018). Figure 7a illustrates CO conversion efficiency with various metals on CeO_2-support catalyst.

It is evident that among all the catalysts, Ni supported on CeO_2 shows the highest CO conversion (Figure 7a). However, nickel-based catalyst (Figure 7b) are more selective to methane formation and therefore, further catalyst modifications are necessary to inhibit methanation. Interestingly, the size of nickel was also shown to play an important role in the conversion of CO. Nickel with a particle size of about 2.9 nm, corresponds to the highest observed activity (Figure 7c). Although, it is expected that a reduction in particle size, reduces the coordination and leads to an increase in volume-to-surface ratio which should ideally increase the activity, the result from Figure 7c implies a different mechanism. X-ray absorption fine structure (XAFS) in combination with transmission electron microscopy (TEM) studies revealed that besides the metal surface, the interface of metal and the supporting oxide (i.e. Al_2O_3) plays a crucial role in enhancing the activity, and should be optimised to improve catalytic conversion (Kitagawa et al., 2014).

More recently, there have been reports of significant promising research findings on using single-atom and single-atom-alloy (SAAs) catalysts in high-temperature WGS (Mitchell and Pérez-Ramírez, 2020). As this alloy minimises the use of metal, it implies that the utilisation of noble-metal catalysts becomes cost-effective and comparable with metal oxide-based catalysts. In the last couple of years, bimetallic SAAs, such as Fe/Pd, Fe/Pt, Pt/Au, Ir/FeO_x, Pt/TiO_2 and Au/CeO_2, have been studied in high temperature WGS wherein, an increase in activity by an order of magnitude compared to nanoparticles has been observed (Aragao et al., 2018, Leoni and Wainwright, 2011, Palma et al., 2020, Hannagan et al., 2020, Liang et al., 2020). Based on experimental and theoretical studies, the reaction mechanism was found to be different in SAAs compared to nanoparticles, which affected the activity, stability, turnover frequency and also, hydrogen yield.

Waste-Gas Shift Reactions' Kinetics

The micro kinetics of WGS reactions over metal oxides has been broadly categorised into:

(1) Regenerative mechanism
(2) Associative mechanism.

In the regenerative mechanism, a redox process is involved where, H_2O is reduced to hydrogen, and CO is oxidised to CO_2. The associative mechanism involves adsorption-desorption models wherein, adsorbed species interacts to form intermediates which then decompose to H_2 and CO_2. High-temperature WGS reactions have been explained in terms of regenerative mechanism whereas, in low-temperature WGS reactions, both regenerative and associative kinetics have been shown to take place. Various elementary intermediate steps have been proposed by different authors for the microkinetic model which have been extensively used recently in theoretical calculations to predict possible catalysts that can enhance the kinetic reactions (Fishtik and Datta, 2002, Callaghan et al., 2003, Smith R J et al., 2010, Motagamwala and Dumesic, Jan. 2021).

Table 1
Kinetic relationships for high-temperature WGS reactions.

Model	Kinetic Expression
Kodama	$r = \frac{k[[CO][H_2O] - \frac{[CO][H_2]}{K}]}{(1+K_{CO}[CO]+K_{H_2O}[H_2O]+K_{CO_2}[CO_2]+K_{H_2}[H_2])}$
Hulburt-Vasan	$r = \frac{k[H_2O]}{(1+K[H_2O]/[H_2])}$
Langmuir-Hinshelwood model	$r = \frac{kK_{O_2}K_{H_2O}[[CO][H_2O] - \frac{[CO][H_2]}{K}]}{(1+K_{CO}[CO]+K_{H_2O}[H_2O]+K_{CO_2}[CO_2]+K_{H_2}[H_2])}$
Oxidation-reduction model	$r = \frac{k_1k_2[[CO][H_2O] - \frac{[CO][H_2]}{K}]}{(k_1[CO]+k_2[H_2O]+k_{-1}[CO_2]+k_{-2}[H_2])}$
Bohlboro et al	$r = kP_{CO}^aP_{H_2O}^bP_{CO_2}^cP_{H_2}^d$

Table 2
Kinetic relationships for low-temperature WGS reactions (van Herwijnen and de Jong, 1980).

Model	Kinetic Expression
Campell model	$r = k\frac{P_{CO}P_{H_2O}(1-\beta)}{(1+K_{CO}P_{CO}+K_{H_2O}P_{H_2O}+K_{CO_2}P_{CO_2}+K_{H_2}P_{H_2})}$
Shchibrya model	$r = \frac{kP_{CO}P_{H_2O}(1-\beta)}{(AP_{H_2O}+P_{CO_2})}$
Moe	$r = kP_{CO}P_{H_2O}(1-\beta)$
Kulkova and Temkin	$r = kP_{CO}(\frac{P_{H_2O}}{P_{H_2}})^{0.5}(1-\beta)$

From a macro kinetic model perspective, a number of models exist which can be used in both high- and low-temperature WGS processes. The most common models which are used for high-temperature WGS reactions are listed in Table 1. As the equilibrium constants vary with temperature, the complete listing of the numerical values is described in the catalysts handbook by Twigg (Twigg, 1989).

In general, Langmuir-Hinshelwood model (Table 1) represents the associative mechanism. Similarly, macro kinetic expression for low-temperature WGS reactions also exists. Some of the widely used equations are represented in Table 2. The micro and macro kinetic models depend on the properties of the catalysts used, including the catalyst particle size, reaction temperature, and metal/metal oxide interface.

A comprehensive list of various micro and macro kinetic approaches that can be used in different catalytic systems has been published re-

cently (Smith R J et al., 2010, Saeidi et al., 2017). It is noticeable that although different rate models have been used to conform the experimental data, most of the kinetic relationships follow the power law kinetic model.

In the following section, we have reviewed the most recent advancements in process synthesis and optimisation within SE-SMR.

CO_2 Sorbents Employed in SE-SMR Processes

CO_2 absorption by solid sorbents is an important step in the reformer of SE-SMR process for high-purity hydrogen production. A highly efficient sorbent for in-situ CO_2 capture during the SE-SMR process should have the following properties: thermal stability at high operating temperatures of the reformer (450-700˚C); high CO_2 sorption/desorption capacity and kinetics; long-term cyclic stability and low costs (Shokrollahi Yancheshmeh et al., 2016). CaO-based materials are the most popular CO_2 sorbents in the SE-SMR process due to the low raw material cost, environmentally benign and adequate CO_2 capacity and reaction kinetics. Other investigated high-temperature sorbents are lithium zirconate (Li_2ZrO_3) (Peltzer et al., 2018, Liu et al., 2019), sodium zirconate (Na_2ZrO_3) (Ji et al., 2017, Munro et al., 2020), and lithium silicate (Li_4SiO_4) (Wang et al., 2021, Wang et al., 2019). While, the cost of lithium-containing ceramic sorbents limits these sorbents for large scale applications. Na_2ZrO_3 is an attractive option for CO_2 capture due to the lower cost than Li-based sorbents, its fast kinetics and minimal decay in CO_2 uptake capacity, despite the lower CO_2 uptake capacity of Na_2ZrO_3 than that of CaO (Ji et al., 2017, Munro et al., 2020).

The main drawback of CaO-based sorbents is rapid decays in CO_2 sorption capacity over multiple cycles due to the sintering deactivation, which includes the agglomeration of small particles, the change of pore shape, and the shrinkage in pore size, as well as reacting with the sulphur containing gases to form $CaSO_4$ (Shokrollahi Yancheshmeh et al., 2016). To improve the performance of CaO-based sorbents for CO_2 capture, extensive research has been conducted such as using different precursors for CaO-based sorbents synthesis; stabilisation of sorbents by support materials (aluminium, magnesium and zirconium oxides), and reactivation of sorbents with hydration, thermal and chemical pretreatment (Shokrollahi Yancheshmeh et al., 2016, Erans et al., 2016, Dou et al., 2016).

In the most of SE-SMR studies, simple physical mixing patterns of sorbent and catalyst are applied. Recently, a novel approach that involves the combination of a reforming catalyst within the solid sorbents (CSCM: combined sorbent catalyst materials) has been proposed, which has the benefits of enhancing the mass transfer and reaction kinetics, preventing the particle segregation in the fluidised bed reactor, and promoting the material reprocessing to decrease the production cost (di Felice et al., 2019). Xu et al. (Xu et al., 2016) produced Ni/CaO-$Ca_5Al_6O_{14}$ extrudates and investigated it under the SE-SMR conditions. The result indicated that the $Ca_5Al_6O_{14}$-stabilised bifunctional catalyst showed high stability and CaO utilisation efficiency than that of Ni/CaO. García-Lario et al. (García-Lario et al., 2015) investigated the performance of a hybrid material that was synthesised through the mixing of CaO, NiO and calcium cement aluminate under the SE-SMR, and the results exhibited that the hybrid material could achieved a stable CO_2 carrying capacity of 20 wt.% of the total weight of CaO with the H_2 composition over 94 vol.% (dry basis). Di Giuliano et al. (di Giuliano et al., 2017) synthesised a Ni-CaO-mayenite CSCM by wet mixing and impregnation methods, and characterised by XRD, BET/BJH, SEM/EDS, and TPR. It showed the CaO load in CSCM affected the CO_2 capture and reforming performance, and the presence of mayenite could be an inert binder to prevent the sintering of CaO. Later on, the authors studied the performance of CSCM in multicycle SE-SMR/regeneration at atmosphere in a packed-bed reactor, and the results indicated that the catalytic activity of Ni was not reduced in the CSCM but the CO_2 sorption capacity was decreased over cycles. It was suggested the simple and highly stable support materials were recommended to improve the multicycle performance of combined materials (di Giuliano et al., 2019).

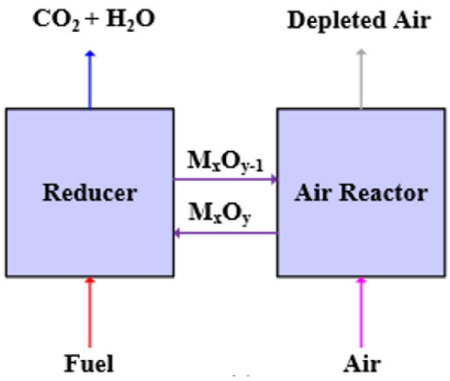

Figure 8. Simplified schematic of chemical looping combustion process (Bahzad et al., 2019).

In conclusion, cost-effective sorbents or CSCM play a key role in deployment of SE-SMR process in a large scale. However, the combined sorbent with catalyst materials for SE-SMR have lots of potential advantages, further work of the life cycle performance of the catalyst and sorbent as well as the physical strength, attrition resistance, and sulphur tolerance of the material are still required. Moreover, the materials should be tested under the pressure and and over a wider range of operating conditions in lab- or pilot scale reactors to broaden its possible field of application.

Advanced Process Configurations for SE-SMR

Sorption-Enhanced Steam-Methane Reforming - Integrated with Chemical Looping Combustion (SE-SMR + CLC)

The high energy demand associated with SE-SMR processes is considered a key drawback in large-scale deployment of SE-SMR processes. In order to the energy intensity of the process, a new configuration of SE-SMR process has been proposed by integrating this process with chemical looping technology. The chemical looping combustion technology (CLC) is a promising technology that aims to mitigate the carbon emissions by using an oxygen-donor material to combust the fuel instead of atmospheric air (Fan et al., 2012) .

The SE-SMR+CLC process comprises two process units. First, compressed methane is fed with steam to the reformer along with the CaO (i.e the CO_2 adsorbent generated in the calciner), where Eq. 7 takes place (Tzanetis et al., 2012). The reformer discharge gas stream is then sent to a condenser where water is removed and a high-purity hydrogen is produced. The calcium carbonate solid formed *via* carbonation reaction is discharged and decomposed to CaO in the calciner by utilising the heat liberated from the air reactor in the CLC process - Eq. 8 (Abbas et al., 2017). The second process unit includes of the CLC process. The CLC process is made up of two individual reactors: fuel and air reactors. In the fuel reactor, metal oxide is used to fully combust the fuel fed resulting in a mixture of carbon dioxide and steam. The metal oxide originating from this reactor is next regenerated within the air reactor as illustrated in Figure 8 (Bahzad et al., 2019). The reactions taking place in the fuel and air reactor are represented by Eq. 7 and Eq. 8 (Zhu et al., 2015).

$$\text{Fuel reactor}: C_nH_m + \left(2n + \frac{m}{2}\right)MeO \rightarrow nCO_2 + \frac{m}{2}H_2O + \left(2n + \frac{m}{2}\right)Me \quad (7)$$

$$\text{Air reactor}: O_2 + 2Me \rightarrow 2MeO \quad (8)$$

Part of the heat generated in the air reactor is supplied to the fuel reactor to facilitate the corresponding endothermic reaction. Some of the generated heat is integrated with the calciner.

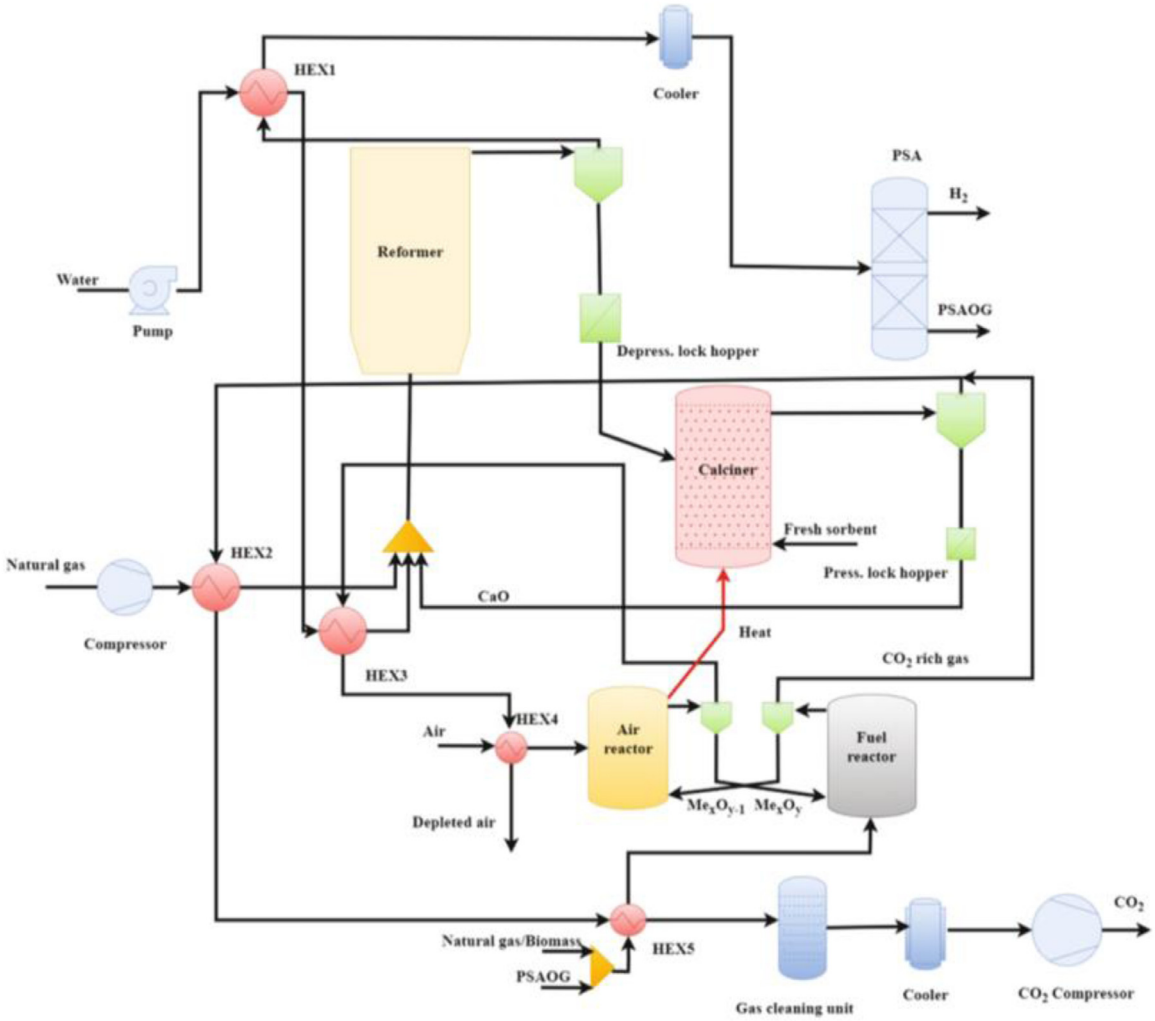

Figure 9. Process Flow diagram for SE-SMR + CLC process (Yan et al., 2020).

The carbon dioxide formed in the fuel reactor is dried and compressed for storage. Therefore, the integrated SE-SMR-CLC process not only helps to capture CO_2, but is also improves the SE-SMR efficiency (Fan and Zhu, 2015).

In the majority of the research that has investigated SE-SMR+CLC processes, Ni-based materials have been used as an oxygen carrier, with methane serving as the fuel used in the fuel reactor in the CLC process. This configuration was first proposed by Zhu et al in 2014 (Zhu and Fan, 2015). Ni-based oxygen carrier is employed due to its favourable tendency to exchange oxygen between the fuel and the air reactors. It is also associated with the desirable amount of thermal energy released when oxidised with air in the air reactor (Zhu et al., 2015, Alam et al., 2017). This process was further modified by optimising the operating condition including reformer, calciner, fuel and air reactors' temperature, steam-to-methane and CaO-to-steam ratios (Zhu et al., 2015). Also, the thermal energy of the process was optimised by coupling it with a heat recovery steam generator (HRSG) unit and gas/steam turbines to generate power – rendering a self-sustained process (Fan and Zhu, 2015, Alam et al., 2017). Cu-based materials have also been studied in a three -stage transient process developed by Fernandes et al. (Fernandez et al., 2012, Fernández et al., 2012). This process is composed of sorption-enhanced reforming to generate a concentrated H_2 gas product with a purity of 95 vol% on dry basis using Ca/Cu mixed metal oxide. The process is then coupled with a pressure swing adsorption (PSA) unit to yield a >99% purity hydrogen (Fernández and Abanades, 2017). The Cu here is considered as an inert. The next stage is to oxidise Cu to CuO with a diluted air stream (low O_2 concentration) fed at a low temperature in order to avoid the calcination reaction. The final temperature of the bed at this stage is well below the calcination reaction (i.e. 300 °C) thus, an intermediate heating step is added by circulating the O_2-depleted stream at the end of the oxidation step to integrate its excess heat with the bed. This process has been further improved by combining the PSA off gas with the syngas produced from the last stage to increase the temperature of the bed, and to prepare it for the calcination step (Fernández and Abanades, 2017). The process then continues with the reduction of CuO to Cu. The heat generated during the reduction is integrated with the calcination reaction. Finally, the steam-methane reforming takes place as the last stage where the heat released throughout the previous stage is utilised. It is mentionable that due to the endothermic nature of the SMR reactions, the bed temperature decreases to the required SMR temperature in preparation for the next cycle.

In other studies, the usage of iron-based oxygen carriers in the SE-SMR+CLC process has been investigated. Fe-based oxygen carriers have been successfully employed in different pilot plants along with different fuels, such as biomass, methane and flue gases. Also, the use of biomass as fuel in the CLC process has been evaluated in other studies (Yan et al., 2020). Sensitivity analyses have been performed to determine the optimum operating conditions with systems using Ni-based oxygen carriers (Yan et al., 2020, Fernández and Abanades, 2017). In addition, the thermodynamic performance of the iron-based metal oxides shows a simi-

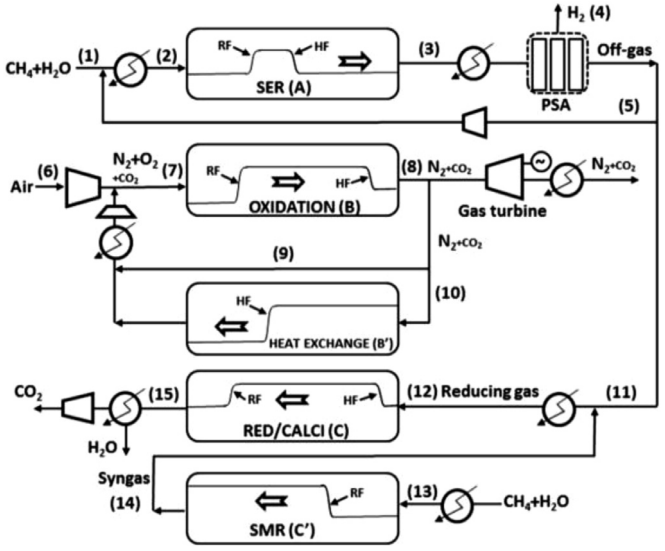

Figure 10. Ca/Cu chemical looping sorption enhanced reforming process flow diagram (Fernández and Abanades, 2017).

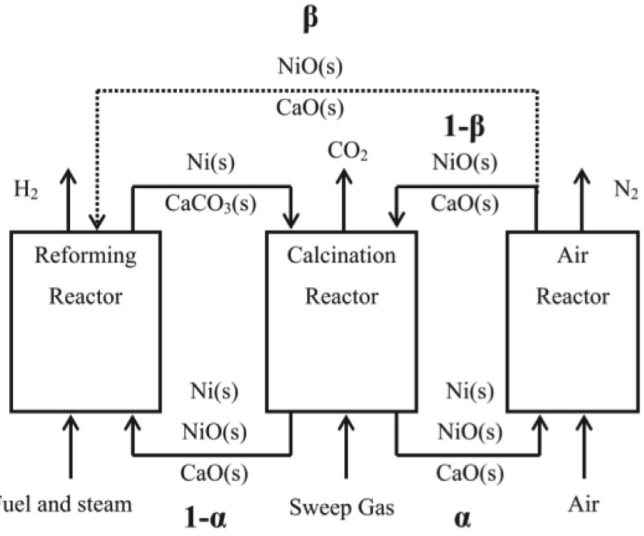

Figure 11. Process flow diagram of sorption enhanced chemical looping reforming process (Udomchoke et al., 2016).

larity in energy penalty, hydrogen purity and overall process efficiency. However, it differs in terms of CO_2 capture rate and fuel conversion, where Fe-based oxygen carriers have demonstrated a 100% fuel conversion i.e. 1.4% higher compared to their Ni-based counterparts (Yan et al., 2020). Figs. 9 and 10

Sorption Enhanced Chemical Looping Reforming Process (SE-CLR)

In this process, methane reforming and the reduction of oxygen carrier represented by Eq. 9-12 are carried out in one reactor i.e the reformer. A hydrogen-rich stream is produced in the reformer. The reduced oxygen carrier is then regenerated in the second reactor (regenerator 1) *via* Eq. 13-15 at a temperature lower than the calcination reaction to avoid the dilution of CO_2 with nitrogen. A third reactor (regenerator 2) is used to decompose the calcium carbonate to calcium oxide and CO_2. The reactions taking place in the reformer and regenerator are listed below (Antzara et al., 2014):

$$\text{Reformer}: CH_4 + MeO \rightarrow CO + 2H_2 + Me \quad (9)$$

$$CH_4 + 4MeO \rightarrow CO_2 + 2H_2O + 4Me \quad (10)$$

$$CO + MeO \rightarrow CO_2 + Me \quad (11)$$

$$H_2 + MeO \rightarrow H_2O + Me \quad (12)$$

$$\text{Regenerator 1 (Air is the oxidising agent)}: Me + {}^1/_2O_2 \rightarrow MeO \quad (13)$$

$$\text{Regenerator 1 } (CO_2\text{is the oxidising agent}): Me + CO_2 \rightarrow MeO + CO \quad (14)$$

$$\text{Regenerator 1 } (H_2O\text{ is the oxidising agent}): Me + H_2O \rightarrow MeO + H_2 \quad (15)$$

The heat required for the calcination reaction is supplied *via* different approaches such as the combustion of fuel in a furnace, or the exothermic heat from the 2nd reactor, depending on the type of oxygen carrier, oxidising agent used in the regenerator 1, or the sweep gas used in regenerator 2. A schematic diagram of illustrating these processes is shown in Figure 11.

The thermodynamic assessment of this process was first carried out in the year 2015 (Antzara et al., 2014). The authors probed into the hydrogen yield/purity, and the thermal energy demand per kmol of H_2 produced. The results were then compared against conventional SMR as well as SE-SMR processes. The effects of the employment of different gases used for oxidation in regenerator 1, and calcination in regenerator 2, on the thermal energy demand and hydrogen yield were also reported in this work. In another study, the impact of splitting the regenerated Ni-based metal oxide from the air reactor on the process thermal efficiency was studied (Phuluanglue et al., 2017). In this work, $CaCO_3$/Ni mixture discharged from the reformer was introduced to the calciner to regenerate CaO *via* the calcination reaction. The CaO/Ni solid mixture was then fed to the air reactor to help oxidise Ni to NiO. A part of the NiO/CaO mixture discharged from the air reactor was recycled back into the reformer, while the rest of this stream was fed to the calciner to exploit its thermal energy in the calciner. A part of the CO_2 exhaust from the calciner, was used as the sweep gas. The remaining part was discharged for sequestration. Any additional heat required by the calciner was supplied by combusting methane with air in the furnace. This process configuration was analysed to obtain the optimum operating condition. The associated thermodynamic performance was also assessed - the details of which are described in the following section.

Other Sorption-Enhanced Steam Reforming Processes

Sorption-enhanced chemical looping reforming is integrated with chemical looping water splitting process (CLWS) to form a SE-CLR-WS process represented by Figure 12. Chemical looping water splitting is a chemical looping process during which three main components i.e. H_2, CO_2 and N_2 are produced (Katayama et al., 2020). The SE-CLR-WS process comprises three stages; first, fuel and steam are fed to the fuel reactor, where Eq. 16 and Eq. 17 take place. The H_2-rich syngas is the first product in the process. The wustite ($Fe_{0.947}O$)/$CaCO_3$ formed in fuel reactor are fed to the second stage, i.e. the steam reactor, where $Fe_{0.947}O$ is oxidised - using steam - to Fe_3O_4, with $CaCO_3$ acting as an inert. Hydrogen is then generated and considered as the main product of this process. Finally, the $CaCO_3$ is calcined to CaO and the solid mixture is recycled to the fuel reactor (Saithong et al., 2019).

$$\text{Fuel reactor}: 4.807Fe_3O_4 + CH_4 \rightarrow 15.228\ Fe_{0.947}O + CO_2 + 2H_2O\Delta H = 518.5\frac{kJ}{mol}, \quad (16)$$

$$\text{Steam reactor}: 3.808\ Fe_{0.947}O + H_2O \rightarrow 1.202Fe_3O_4 + H_2\Delta H = -88.1\ kJ/mol \quad (17)$$

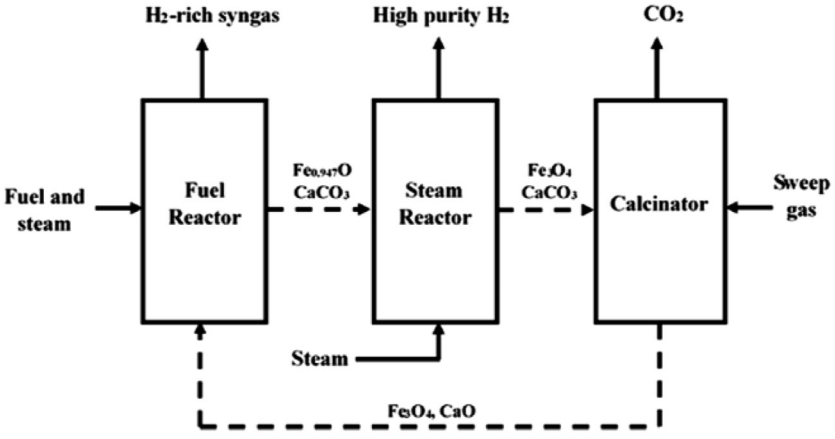

Figure 12. Schematic diagram for SECLR-WS process (Saithong et al., 2019).

Table 3
Comparison between various types of SE-SMR process.

Process	Thermodynamic efficiency	Advantages	Disadvantages	Hydrogen production cost ($/kg H_2)
SE-SMR+CLC (Ni-based OC)	80 – 94%	High efficiency, High H_2 purity	High oxygen carrier cost	-
SE-SMR+CLC (Cu-based OC)	77%	High CO_2 capture%	Low H_2 purity	-
SE-SMR+CLC (Fe-based OC)	71 - 75%	Low oxygen carrier cost	More separation units needed for ultra-pure H_2	3.1 – 3.4
SE-CLR	87 – 91%	High thermodynamic efficiency, high H2 purity	High oxygen carrier cost, low CO_2 capture %	-
SE-CLR-WS	30 - 68%	Inherent CO_2 capture, less separation steps toward ultra pure H_2	Low thermodynamic efficiency	-
SE-SMG	-	Carbon zero or negative emission.	High energy penalty	-

*Ultra pure H_2 means an H_2 purity of ≥99%

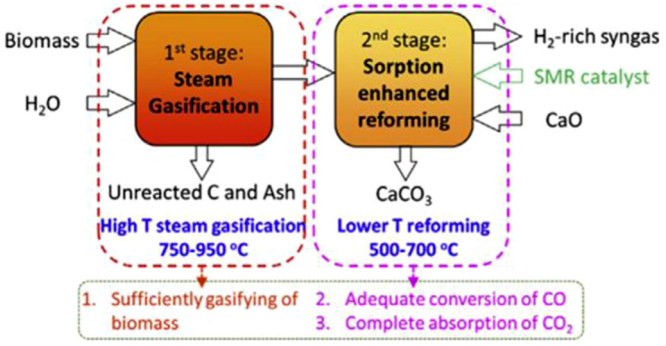

Figure 13. Schematic diagram of staged sorption enhanced reforming of biomass (Li et al., 2020).

The effects of steam-to-fuel ratio, CaO-to-CH_4 and Fe_3O_4-to-CH_4 ratios on the process efficiency were determined and reported in the literature (Saithong et al., 2019).

A novel sorption-enhanced staged gasification (SE-SMG) of biomass has been also proposed (Li et al., 2020). This process consists of two stages. Here, biomass is initially gasified, leading to the formation of syngas, methane, ash and tar. The solids are separated, while the gaseous stream is fed to the sorption-enhanced reformer where a rich H_2 product is generated. This process has the advantage over its single-stage biomass sorption-enhanced reforming counterpart, since it is more *convenient* to operate the reformer with gaseous products, compared with the presence of combined solid and gas phases (Li et al., 2020) .

A comparison between different processes in terms of thermodynamic efficiency, potentials and setbacks and economic feasibility is given in Table 3:

Techno-economics of SE-SMR: *A Scrutiny!*

In a conventional SMR process, the generated syngas (containing almost 12% CO), in a packed-bed reactor filled with an Ni-based catalyst, would need to be further processed in order to convert CO to CO_2 (Diglio et al., 2017). This means that the reformer and shift reactors must be followed by a CO_2 separation unit (normally an amine absorption unit, or a pressure swing column) (Diglio et al., 2017). These additional units may account for 35% of the total capital cost of a conventional SMR process (Berghout et al., 2013). These additional units may also lead to the reforming process efficiency drop by 6-10% (Zhu and Fan, 2015). As discussed earlier, an SE-SMR process is inherently an intensified process which allows for a more compact process unit (since the catalyst and adsorbent, normally CaO, are placed together inside one reactor), ultimately resulting in total process cost reductions. The choice of reactor, whether a more investigated fluidised-bed, or a fixed-bed reactor, could have an impact on the process CAPEX and OPEX. Diglio et al. (Diglio et al., 2017) investigated the techno-economic of an SE-SMR in a network of fixed reactors, with the production of pure CO_2. The synthesised process used part of the generated hydrogen to fuel the endothermic reforming reaction in an 8 packed-bed process unit. The authors found a strong link between the total CAPEX and the reactor network; hence, the optimisation of operating variables is highly important in order to minimise the number of the reactors. This leads to a reduction in total CAPEX. The share of various process units in the total costs of the SE-SMR process is illustrated in Figure 14.

The calculated hydrogen and CO_2 avoided costs were realised to be 1.6 and 29.85 €/kg, respectively, which are 33% and 40% lower than the conventional SMR with a standalone carbon capture unit. The analysis also revealed a strong link between the economic performance of the SE-SMR process and the fuel cost. As of today, the TRL of SE-SMR for hydrogen production is estimated to be at 4, incentivising significant research to accelerate further developments of advanced sorbents,

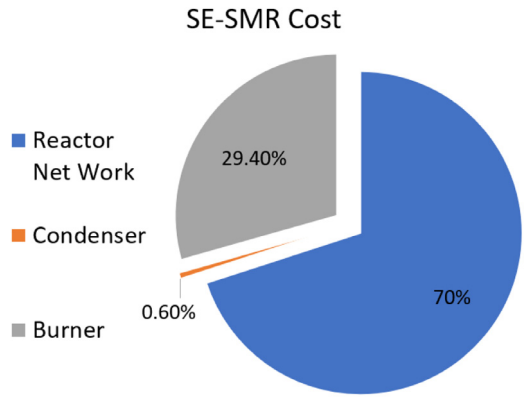

Figure 14. The share of various process units in the total SE-SMR cost (Diglio et al., 2017).

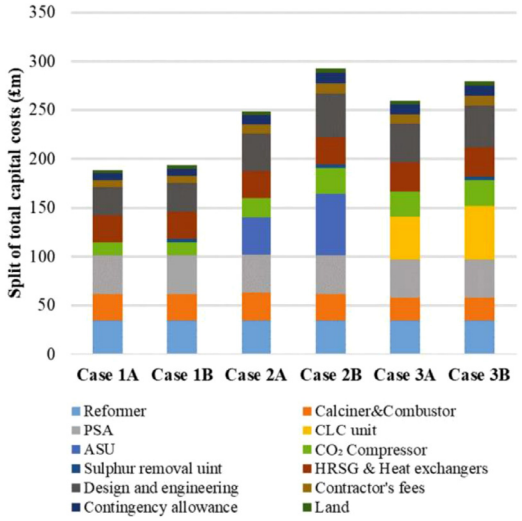

Figure 15. The costs breakdown of the 6 different synthesised SE-SMR processes (Yan et al., 2020).

catalysts, as well as improved reactor designs, system integration and optimisation. As a result, more recently, Yan et al. (Yan et al., 2020) investigated the techno-economics of 6 different SE-SMR configurations integrated with indirect natural gas or biomass-fired calciner, oxy-fuel combustion and chemical looping combustion for large-scale low-carbon H_2 production based on their previous studies (Yan et al., 2020) on the thermodynamic performance of these processes. The authors learnt that the employment of biomass to indirectly heat the calciner would be advantageous over its gas-fired counterpart in all the 6 scenarios studied in terms of carbon capture. However, biomass integration led to 8.3% points drop in average process efficiency. The cost breakdowns for the 6 studied scenarios are described in Figure 15.

Similar to Diglio et al's finding, the authors here also reported that the cost of biomass and natural gas as calciner fuels, would have a major impact on the economic performance of the process, which was followed by net efficiency, total direct capital costs of equipment and CO_2 storage costs. The calculations made by these authors suggested that with a selling H_2 price of £3.00/kg, the investment in any of the 6 investigated synthesised processes would be paid back after only 8 years and with a no-carbon-tax assumption.

Quite recently, Lee at al. (Lee et al., 2021) carried out a comparative techno-economic analysis in a novel sorption-enhanced Pd-based membrane reactor (SEMR) as the next generation technology for combined carbon capture and high-purity hydrogen production. The authors simulated a packed-bed reactor (PBR), membrane reactor (MR), as well as an SEMR process in aspen Plus to probe into the thermodynamics of their synthesised units. The developed model comprised the reforming, WGS and CO_2 adsorption with CaO adsorbents due to its low cost and high reactivity. The authors calculated the costs associated with H_2 production *via* the 3 studied processed to be 4.53, 1.98 and \$3.04/kg_{H2} for PBR, MR and SEMR, respectively; however, the SEMR was considered to be the preferred process due to the considerably lower CO_2 emission rates.

Artificial Intelligence in SE-SMR Processes

As with all fields in recent years, the use of artificial intelligence (AI) has expanded and opened up the potential to develop the SE-SMR process, including the selection of catalysts and sorbents, and the prediction of operating performance. These abilities could lead to faster scale up, safer operation, cheaper and more sustainable or active materials and may even lad to cost reductions. Within this section we will explore these opportunities to utilise AI and machine learning (ML) for the SE-SMR process in greater depth, covering catalyst and sorbent development, and process predictions. A set of best practises in ML for chemistry applications, which broadly covers catalyst and sorbent design and selection has been published recently and could be utilised as a reference source for others looking to start in this field.

Catalyst and Sorbent Design and Screening

As has been demonstrated within this manuscript and within the literature, the selection of optimised catalysts and sorbents for the SE-SMR process is critical for ensuring effective operation. One of the keyways in which AI can support this development further is by quantitative structure-property/activity relationship (QSPR/QSAR) models. These models create links between properties of molecular descriptors with behaviours/properties of those materials, which in turn can be utilised to predict the behaviours/properties of new materials for which experimental or modelling data would be too time consuming or expensive to produce. An excellent general overview of QSAR is presented by Muratov et al. (Muratov et al., 2020). There is also a paper instructing researchers how not to do QSAR/QSPR modelling (Dearden et al., 2009). The use of Machine Learning algorithms coupled with *In Silico* quantum mechanical Density Function Theory (DFT) calculations offers a faster and higher throughput route to achieving quantitively superior catalysts and sorbents and isn't limited by the short comings of experimental research and its associated errors (Zahrt et al., 2019, Goldsmith et al., 2018).

Much research has however been undertaken using ML to aid the development of heterogeneous catalysts and Metal Organic Frameworks as a CO_2 sorbent, including: ethanol decomposition (Saxena et al., 2020), synthesis of oleochemical carbonates (dos Santos et al., 2020), propylene polymerization (Achary et al., 2016), MOFs for CO_2 capture (Fernandez et al., 2014) (we provide only one key reference here yet are aware there are 10's of other articles on this topic), zeolites for CO_2 capture (Banerjee et al., 2008), oxidative coupling of methane (Takahashi et al., 2018), performance of metal oxides as oxygen carriers (Yan et al., 2020) and methanol electro-oxidation (Li et al., 2017).

Close to SE-SMR, Artrith et al. have utilised ML and DFT to determine new bi-metallic catalysts for ethanol reforming (Artrith et al., 2020). This research highlighted that out of 248 hypothetical catalysts, just four were shown to be promising candidates for this process, including: Cr–Pt–Pt(111), Mn–Pt–Pt(111), Co–Pt–Pt(111), and Zn–Pt–Pt(111).

Whilst not a ML algorithm in its own right, the UBI-QEP (unity bond index-quadratic exponential potential) method is one of the most important computational advances in catalyst screening to date (Shustorovich and Sellers, 1998). Utilising quantum mechanical methods like DFT to determine adsorption energies, adsorbate binding energies, and activation energies is very computationally expensive, the UBI-QEP method significantly reduces this by making a series of statically

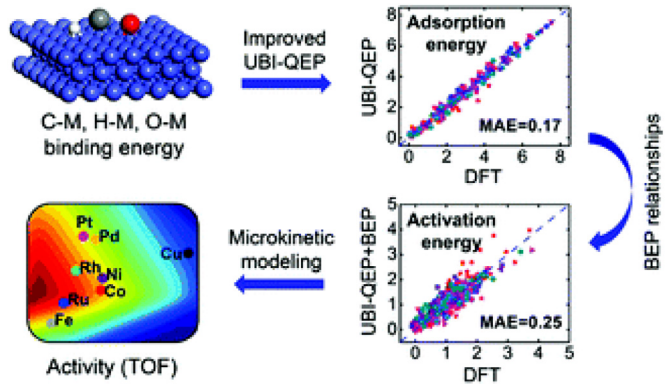

Figure 16. Utilisation of the UBI-QEP method for Steam Methane Reforming to simplify computational design of catalysts (Wang et al., 2019).

sound assumptions and simplified calculations. This has been demonstrated by Wang et al. for the SMR process to aid computational catalyst design (shown in Figure 16) and reduce computational time by 6 orders of magnitude and maintaining accuracy of results similar to that of DFT (Wang et al., 2019).

Within the work by Saxena et al. (Saxena et al., 2020) on ML prediction of catalysts for ethanol decomposition and non-oxidative dehydrogenation reactions they developed an understanding of the most important molecular descriptor features and these features correlate between each metal atom in the catalyst lattice. In addition, they explored the impact of varying the ratio of testing and training data, showing that the error increased as the ratio of testing/training data increased. This is shown within Figure 17 and highlights the need for having a large amount of training data to ensure representative predictions.

As shown within this section, at present, there is not a significant amount of research that has been conducted using AI to improve the design and selection of catalysts and sorbents for SE-SMR, especially for the sorbents and these are definitely areas where further work should be performed by researchers. The potential of AI to deliver cheaper, more effective, more sustainable catalysts and sorbents for SE-SMR with less computational or person effort is tangible and easily within the bounds of current research capabilities. Nevertheless, a 'grain of salt' approach must be taken with these AI predictions as it is possible to predict catalysts / sorbents which are un-synthesisable or where the synthesis technique has a greater influence on the final material activity compared to the fundamental predicted properties of the materials components.

Predicting the Performance of SE-SMR

Modelling techniques including Aspen Plus and gproms have quite rightly become a first port of call when studying a process or designing a new plant. These models utilise thermodynamic and kinetic data to predict the outputs of a process and can be used to validated experimental data. However, they are time consuming to set up and execute, furthermore depending on the complexity of the model can be highly specialised for one set of operating conditions / process configuration and are thus not adaptable. The use of ML algorithms in replacement of these models offers a lower cost solution that is adaptable and retrainable. These ML models can also be utilised 'on-stream' on live processes to confirm operational performance criteria are being reached and suggest routes for improved outputs.

Nkulikiyinka et al. have utilised random forest and neural network ML algorithms to predict the performance of SE-SMR based on As-

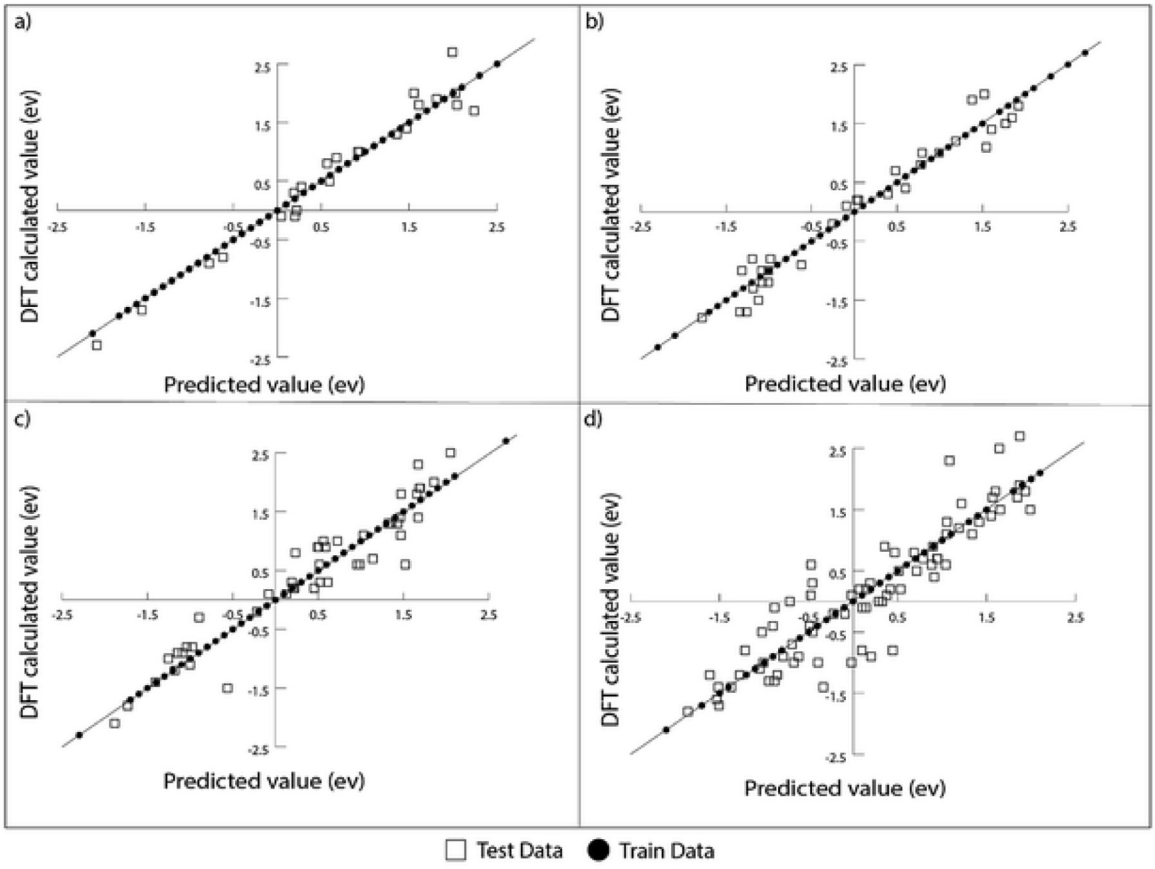

Figure 17. The deviation of DFT calculated oxygen binding energy from that predicted using a gradient boosting regression model for AA terminated A3B bimetallic alloy for (a) a test/train ratio of 15/85, (b) a test/train ratio of 20/80, (c) a test/train ratio of 30/70 and (d) a test/train ratio of 50/50 (Saxena et al., 2020).

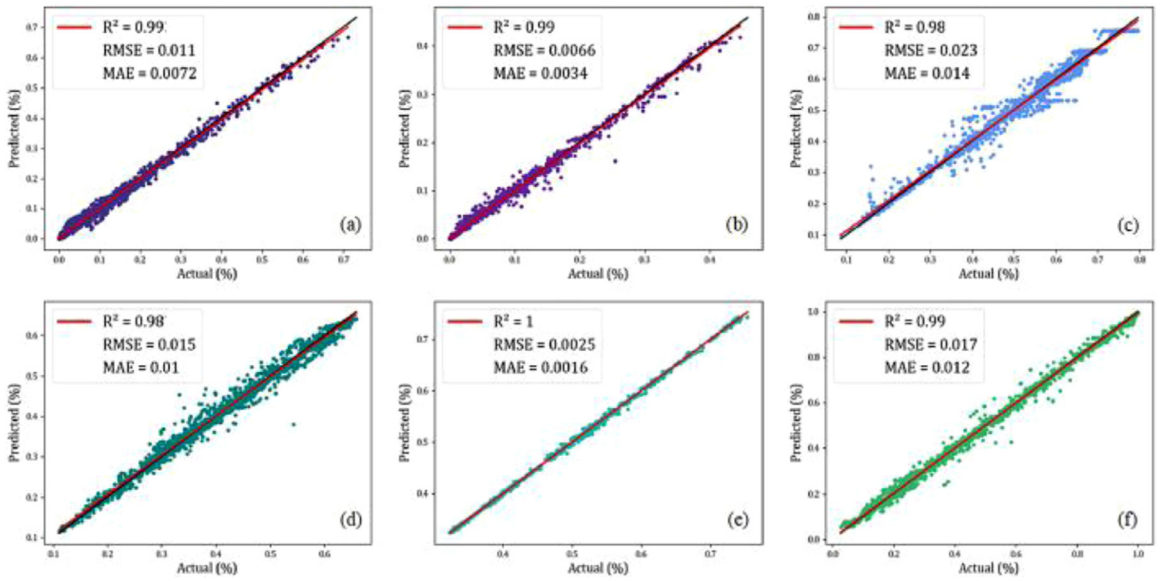

Figure 18. Actual vs predicted plots for a random forest algorithm predicting outputs from a SE-SMR process: a) reformer [H2O], b) reformer [CO], c) reformer [H2], d) regenerator [H2O], e) regenerator [CO2], f) reformer CH4 conversion modelled. Black lines in each figure represent y = x. Red lines indicate the line of best fit (Nkulikiyinka et al., 2020).

pen Plus data, the accuracy of one of these models is reflected in Figure 18 (Nkulikiyinka et al., 2020). These models essentially operated as surrogates that could be implemented 'on-stream' for live predictions of theoretical maximal performance within a process. Going one step further, Alsaffar et al. (Alsaffar et al., 2020) utilised experimental data on CO_2 methane reforming produced by Fan et al. (Fan et al., 2011) and fitted the data to an Artificial Neural Network (ANN) to predict the H_2 yield and CH_4 conversion. Whilst their analysis and interpretation of the model was quite simple, the demonstration of ANN's ability to fit to data with inbuild experimental error was useful. A set of surrogate ANN models for the follow-on pressure swing adsorption (PSA) process of SE-SMR was also implemented using Aspen Adsorption based on experimental data and showed that the models can approximate the performance of the PSA process with high accuracy (Yu et al., 2021).

The use of these ML models generated is often questioned in terms of its reproducibility and adaptability to different processes; however, within the work by Krzywanski et al (Krzywanski et al., 2018) it was demonstrated that an ANN model was able to predict H_2 purity with an error of ± 8% using data obtained from two different fluid-bed reactors each operated for sorption enhanced gasification of biomass. Similar work was conducted with a 200 kWth gasifier operating under sorption enhanced conditions for H_2 production (Salah et al., 2016). In this research, a dynamic NN was designed and trained on ~2,500 data points wider over a range of operating conditions than that of Krzywanski et al. (Krzywanski et al., 2018). As such a maximum error of 15% was achieved, though the general trend was observed in the predicted data, this led to a conclusion that more data was required to reduce errors further. This is often the case with experimental data sets, in that they are too small for use and lack a range of operating conditions or do not cover enough features for the model to interpret what is going on.

All used relatively simple ANN's or other algorithms which are often based on data sets with less than 100 input – output pairs. These kinds of models show that AI has some potential in this field but thus far no truly remarkable demonstrations of AI in SE-SMR have been demonstrated. Potentially the requirement for adaptable algorithms is not required, and instead an individual / set of individual algorithms that are highly specialised on a specific plant / reactor are all that are required, this will be tested as new plants implement AI to test its benefits to process control and optimisation of outputs.

Conclusion and Outlook

In this review, we have given an extensive insight into the recent developments in hydrogen production *via* SMR and SE-SMR process coupled with carbon capture. This work has aimed to probe into both the recent development as well as the current challenges and opportunities in this area. The review describes the overall process, catalysts used in the process and its reaction kinetics, CO_2 sorbents used in the process, process configuration details for SE-SMR and its integration with chemical looping combustion, techno-economical calculations, and the integration of artificial intelligence in the process to identify steps needed to improve the SE-SMR process.

Here, we first gave an overview of global hydrogen production using various processes and the need for hydrogen as clean fuel to reduce the dependence of fossil fuels thereby relegating CO_2 emission and tackling climate change issues. This was followed by demonstrating the advantages of SE-SMR over SMR process. The state-of-the-art catalysts and CO_2 sorbents used in SMR and SE-SMR were summarised which included catalyst design, conversion efficiency and reaction kinetics. Owing to the inherently high energy demand associated with SE-SMR, process configuration and optimisation by integrating chemical looping combustion was discussed. Optimisation of materials involved in chemical looping, chemical reactions, reaction temperature, thermal energy of the process along with heat recovery procedures and the use of biomass as fuel was discussed. This was followed by scrutinising the techno-economic aspect of the SE-SMR process. Due to additional unit processes required for CO_2 separation, process efficiency and process costs would be affected and therefore, optimisation of the corresponding process parameters was studied based on various conceptual scenarios, and summarised. Finally, to improve the efficiency and optimise the process parameters of SE-SMR, integrating artificial intelligence into SE-SMR was discussed which involved the employment of AI for screening new catalysts and sorbents which would improve the conversion efficiency and facilitate the prediction of the performance of SE-SMR by using machine learning algorithms.

The future outlook of SE-SMR in combination with CO_2 capture for production of H_2 as a clean fuel is indeed a promising technology. As of today, the key existing challenges for a viable H_2 production of the SE-SMR process comprise:

1 Development of efficient, stable, and cheap catalysts to improve conversion efficiency
2 Optimisation of the associated energy demand in the process
3 Development and implementation of robust heat and energy recovery systems
4 Optimisation of the process configuration through techno-economic and exergy calculations to optimise total production costs

In order to overcome some of these challenges, future research is expected to have a great focus on the development of robust AI and machine learning techniques. Although such techniques are being applied extensively (e.g. in predicting the optimum properties of efficient catalysts), the realistic feasibility of the predictions needs to be validated experimentally. In order to reduce the associated costs, the use of biomass as fuels has also been investigated; however, heat loss in the system is considered yet to be high, hence the need for the development of advanced heat recovery systems. Nevertheless, in order to optimise total production costs, detailed techno-economic and exergy studies are deemed to be highly critical prior to the implementation of SE-SMR processes at scale.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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